RESEARCH PROPOSAL

on

SYNTHESIS OF CARBON NANOSTRUCTURE BASED POLYMER COMPOSITES AND THEIR ELECTRICAL AND PHYSICOCHEMICAL CHARACTERIZATION

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INTRODUCTION

Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future. The new advanced technologies need new materials with improved characteristics, like lower weight, higher resistance to environmental exposures, lower production costs, higher strength and durability. In order to fulfil these requirements, scientists strive to find solutions among more sophisticated materials, *i.e.* composites. Composites are systems "composed" of two or more physically distinguishable components that combine the individual properties of their constituents and yield new features and better performances [1]. Although the concept of composite materials has been known for thousands of years, recent advances in this field are particularly appealing. The origin of the renascence of composites lies in the progress of the synthesis of nano particular materials as fillers, resulting in new properties. Therefore, the today's composites offer a great variety of properties and find numerous applications in various industrial branches, including: aerospace, automotive, electronics, construction, energy, bio-medicine, just to name a few of them. Furthermore, composite materials have improved the properties of a plethora of everyday products.

The high-energy-density capacitors are the promising power source and have attracted considerable attention in recent years. The increasing pollution due to electrical vehicles

and explosive growth of portable electronic devices has pushed the development of high-performance supercapacitors as the urgent requirement. Polymer-based composites with excellent dielectric performance are currently very popular topics in the field of materials science, and have received increasing attention in recent years [2, 3]. Polymers are presently the materials for energy storage applications because of their features such as high electric breakdown field, low dielectric loss, easy processing, and low cost. However, the dielectric constant (k) of common polymers is low (i.e. $k < 3$). Thus, a key issue is to enhance dielectric constant of polymers while retaining other excellent performances. Such composites could be useful as high-energy-density capacitors [4].

LITERATURE REVIEW

High-surface carbons, noble metal oxides, and conducting polymers are the main families of electrode materials studied for supercapacitor applications. Conductive polymers have been extensively studied in supercapacitors. The main conductive polymer materials that have been investigated for the supercapacitor electrode are polyaniline (PANI), polypyrrole (PPY), polythiophene (PTH) and their derivatives, and so on. Among these polymers, PANI is considered the most promising material because of its high capacitive characteristics, low cost, and ease of synthesis. However, the relative poor cycling life restricts its practical applications. Recently, advancement of nanoscale binding technique provides an innovative route to prepare PANI-based composites with better performance as electrode material. It has been demonstrated that PANI composite with metal oxides exhibit improved supercapacitor performance.

Synthesis of Carbon Nanostructure based Polymer Composites and their Electrical and Physicochemical Characterization

Graphene is a two-dimensional form of graphite, the high surface area, excellent mechanical properties and conductivity of this new material have attracted great interests. Graphene oxide, bearing oxygen functional groups on their basal planes and edges, is a single sheet of graphite oxide and exhibits good performance. It can be obtained by exfoliation of graphite oxide. The tunable oxygenous functional groups of graphene oxide facilitate the modification on the surface and make it a promising material for composites with other materials. Recent reports on ultracapacitors based on graphene have attracted great interest. Many graphene composites with conducting polymers have been developed. However, the effect of raw graphite material sizes and feeding ratios on the electrochemical properties of such composites have not been investigated intensively [5].

Cheng Yang et al reported that the multiwall Carbon nanotube (MWCNTs) -polypyrrole (PPy) composites prepared by an inverse microemulsion polymerization. Transmission electron microscopy, X-ray photoelectron spectroscopy and Raman spectroscopy indicated that the MWCNTs were coated with PPy. The composites presented a stable high dielectric constant (~44), rather low loss (<0.07), and large energy density (up to 4.95 J cm^{-3}). Such MWCNT composites can be used to store charge, high-energy-density capacitors and electrical energy and play a key role in modern electronics and electric power systems [4].

Qun Li et al reported that the chemically purified multiwalled carbon nanotube/poly(vinylidene fluoride) (MWCNT/PVDF) composites were fabricated. Raman spectroscopy and transmission electron microscopy micrographs indicated that the catalysts metal particles and amorphous carbon had been removed from the purified MWCNTs. The most important result is that the dielectric constant of the composites is enhanced remarkably, and the dielectric constant of 3600 is obtained in the composite with

8 vol.% purified MWCNT at 1 kHz [6]. E Kymakis et al present a study on the interaction between single-walled carbon nanotubes (SWNTs) and the soluble polymer poly(3-octylthiophene) (P3OT). Composites of SWNTs embedded in the polymer matrix were fabricated by drop casting of the nanotube/P3OT mixture dissolved in chloroform and have been studied using absorption spectroscopy, electrical characterization methods and high-resolution electron microscopy. As the nanotube concentration increases from 0 to 20 wt. %, the conductivity of the resulting films increases by five orders of magnitude [7]. Ranulfo Allen et al suggested a method to align carbon nanotubes with in-situ polymerization of conductive polymer to form composite films and fibers. Use of the conducting polymer raised the conductivity of the films by 2 orders of magnitude. The carbon nanotube/conductive polymer composite films and fibers had conductivities of 3300 and 170 S/cm, respectively. The relatively high conductivities were attributed to the polymerization process, which doped both the SWNTs and the polymer. In-situ polymerization can be a promising solution-processable method to enhance the conductivity of carbon nanotube films and fibers [8]. Chuang Peng et al reported that composites of conducting polymers (CP) and carbon nanotubes (CNT) show improved mechanical, electrical, and electrochemical properties compared with conducting polymers alone, leading to a wide variety of applications including sensors, catalysis, and energy storage. CP–CNT composites combined the large pseudocapacitance of the polymers and the mechanical and structural properties of the nanotubes and are thus highly promising in novel supercapacitors with ultra-high capacitance and power density. Three methods have been developed to prepare CP–CNT composites. Chemical oxidation is a simple, low cost method suitable for mass production. Electrochemical deposition of CPs on CNT preforms

leads to an inhomogeneous structure; as a result, the synergistic effect of the two components is reduced. Electrochemically co-deposited composites have a homogeneous network structure facilitating both electron and ion movements. Therefore, they exhibit greatly improved electrochemical capacitance compared with pure conducting polymers [9]. Ashis K. Sarker et al describes ultrathin film electrode composed of polyaniline (PANi) and electrochemically reduced graphene oxide (ERGO) bilayers, which was achieved using layer-by-layer (LBL) assembly method. The performance of the electrode composed of 30 PANi/ERGO bilayers denoted to PANi-ERGO30 was analyzed in a three-electrode cell using aqueous 1 M H_2SO_4 electrolytes. The electrode exhibited a specific capacitance of 1563 F/cm^3 (at a current density of 3.0 A/cm3). This breakthrough was made possible by the development of a unique process that minimized the morphological damage to the thin film electrodes, and prepared optimal doping and oxidation state of PANi in the multilayer films for achieving excellent electronic conductivities and ionic transport [10]. Nanjundan Ashok Kumar et al reported an alternative and effective route to prepare conducting polyaniline-grafted reduced graphene oxide (PANi-g-rGO) composite with highly enhanced properties. In order to prepare PANi-g-rGO, amine-protected 4-aminophenol was initially grafted to graphite oxide (GO) via acyl chemistry where a concomitant partial reduction of GO occurred due to the refluxing and exposure of GO to thionyl chloride vapors and heating. Electron microscopic studies demonstrated that the resultant composite has fibrillar morphology with a room-temperature electrical conductivity as high as 8.66 S/cm and capacitance of 250 F/g with good cycling stability [11]. Hualan Wang et al reported that Graphene oxide, a single layer of graphite oxide (GO), has been used to prepare graphene oxide/polyaniline(PANI) composite with improved electrochemical performance

as supercapacitor electrode by in situ polymerization using a mild oxidant. The composites are synthesized under different mass ratios, using graphite as start material with two sizes: 12 500 and 500 mesh. The result shows that the morphology of the prepared composites is influenced dramatically by the different mass ratios. The highest initial specific capacitances of 746 F g−1 (12 500 mesh) and 627 F g−1 (500 mesh) corresponding to the mass ratios 1:200 and 1:50 (graphene oxide/aniline) are obtained, compared to PANI of 216 F g−1 at 200 mA g−1 by charge–discharge analysis between 0.0 and 0.4 V. The improved capacitance retention of 73% (12 500 mesh) and 64% (500 mesh) after 500 cycles is obtained for the mass ratios 1:23 and 1:19 compared to PANI of 20%. The enhanced specific capacitance and cycling life implies a synergistic effect between two components. This study is of significance for developing new doped PANI materials for supercapacitors [12]. Qingqing Zhang et al reported that the graphene oxide/polyaniline (GO/PANI) composite was prepared by the one-step electrochemical co-deposition method. The different mass concentrations of GO were utilized to improve the electrochemical performances. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images showed that PANI nanofibers not only were coated on the surface but also intercalated into GO sheets. The maximum specific capacitance of the GO/PANI composite achieved 1136.4 F g−1 with a GO concentration of 10 mg L−1 at a scan rate of 1 mV s−1, which is almost two-fold higher than that of PANI (484.5 F g−1). High electrochemical performances were attributed to increasing active sites for the deposition of PANI provided by large surface areas of GO sheets and the synergistic effect between GO and PANI, shortening the ion diffusion paths. Results indicate that the GO/PANI composites can be developed as excellent electrode materials of high-performance supercapacitor by a

versatile, effective and environment-friendly method [13]. Zhu J et al reported that the Polyaniline (PANI) nanocomposites incorporating different loadings of graphene and various other carbon nanostructures including carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been synthesized using a surface-initiated polymerization (SIP) method. Transmission electron microscopy (TEM) results indicate that the graphene has been exfoliated into a few layers (typically one, two, and three layers) during polymerization and has been uniformly dispersed in the PANI matrix. The graphene layer dispersion degree is quantified by a free-path spacing measurement (FPSM) method based on the TEM microstructures. The SIP method also demonstrates its feasibility for coating PANI on one-dimensional (1D) CNFs and CNTs without introducing additional surface functional groups. The effects of graphene size, loading level, and surface functionality on the electrical conductivity and dielectric permittivity of their corresponding nanocomposites have been systematically studied. More interestingly, negative permittivity is found in each composite which can be easily tuned by adjusting the filler loading, morphology, and surface functionality [14].

Among several methods i.e. arc discharge, laser ablation and chemical vapour deposition (CVD) etc. for preparing CNTs, arc discharge is the most practical for scientific purposes because the method yields highly graphitized tubes due to the high process temperature hence the issues related to large scale and high purity synthesis of CNT by arc discharge are the most important objectives nowadays. However, besides CNTs, arc discharge methods produce many by-products. As a result, the process requires complicated and well controlled purification steps. The synthesis condition, under which the arc discharge is

made, is one of the important key factors affecting the yield and morphology of the CNTs [15,16].

OBJECTIVES

The proposed research work covers the synthesis and characterization of carbon nanostructure based polymer composites to form the basis of new materials and processes of interest for future applications.

The objectives of the proposed research problem will come in shape with following experimental steps:

1. The two dimensional carbon nanostructures Graphene oxide (GO) and/or Reduced Graphene Oxide (RGO) i.e. Graphene will be synthesized.
2. The metal and metal oxide i.e. Pd, Ni, Ti, Sn, NiO_2, TiO_2, SnO_2 etc. doped two dimensional (2-D) carbon nanostructures (GO and/or RGO) will be synthesized.
3. The metal and metal oxide i.e. Pd, Ni, Ti, Sn, NiO_2, TiO_2, SnO_2 etc. doped one dimensional (1-D) Carbon nanotube (CNT) will be synthesized.
4. The carbon nanostructure (undoped and/or doped) - polymer composites will be synthesized using Polyaniline (PANI), Polymethyl methacrylate (PMMA) and/or Polystyrene (PS).
5. The physicochemical structural properties will be analyzed by in situ X-ray diffraction (XRD) and Raman spectra.
6. The morphological properties will be studied using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) Characterization.

7. The electrical properties i.e. dielectric constant, impedance, resistivity, capacitance, tangent loss etc. will be studied.

METHODOLOGY

The objectives of the proposed research problem will come in shape with following experimental steps:

The undoped and doped 1-D & 2-D Carbon nanostructures will be synthesized as following-

1. Preparation of Two Dimensional Carbon Nanostructures:

   The two dimensional carbon nanostructures Graphene oxide (GO) and/or Reduced Graphene Oxide (RGO) i.e. Graphene will be synthesized chemically using Hummer's method and ball milling technique.

2. Preparation of Doped Two Dimensional Carbon Nanostructures:

   The metal and metal oxide i.e. Pd, Ni, Ti, Sn, NiO_2, TiO_2, SnO_2 etc. doped two dimensional carbon nanostructures (GO and/or RGO) will be synthesized by wet chemical co-precipitation method.

3. The metal and metal oxide i.e. Pd, Ni, Ti, Sn, NiO_2, TiO_2, SnO_2 etc. doped one dimensional Carbon nanotube (CNT) will be synthesized using Chemical Vapour Deposition (CVD) or arc-discharge method.

   (a) Preparation of doped carbon electrode:

   The doped carbon electrode will be prepared by mixing the metal and metal oxide i.e. Pd, Ni, Ti, Sn, NiO_2, TiO_2, SnO_2 etc. nanoparticles in different wt% with fine graphite powder using ball milling method. The doped graphite mixtures will palletize in form of small rods (2 inches long and 1mm in diameter) using

hydraulic pressure and then sintered at appropriate temperature for few hours accordingly.

(b) Underwater Arc-Discharge Method:

The underwater DC arc-discharge setup will be developed by connecting the DC power supply to doped carbon electrodes assembly. The power supply will prepare high current diode bridge configuration using low voltage & high current step down transformer.

The electrode assembly will be mounted in small rectangular shape glass box for underwater arc discharge. This rectangular shape glass box will be fixed between the electromagnetic coils to create the magnetic field during underwater arc-discharge.

4. The synthesized products will be purified in the following steps

   (a) Oxidative heating

   (b) Acidic heating

   (c) Vacuum annealing

5. The carbon nanostructure (undoped and/or doped) - polymer composites will be synthesized using in situ chemical polymerization and solution mixing method. Polyaniline (PANI), Polymethyl methacrylate (PMMA) and/or Polystyrene (PS) will be used for preparing polymer composite.

The synthesized undoped and doped 1-D & 2-D Carbon nanostructures will be characterized as following-

6. The physicochemical structural properties will be analyzed by in situ X-ray diffraction (XRD) and Raman spectra.

7. The morphological properties will be studied using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) Characterization.
8. The electrical properties i.e. dielectric constant, impedance, resistivity, capacitance, tangent loss etc. will be studied using impedance analyzer.

Finally a comparative study will be done to draw concrete conclusions.

REFERENCES

1. D. Hull, An introduction to composite materials, Vol. Cambridge Solid State Science Series, Cambridge University Press, Cambridge, 1981.
2. Li JY, Zhang L, Ducharme S. 'Electric energy density of dielectric composites', Appl Phys Lett 90(13) (2007) 132901-3.
3. Chu B, Zhou X, Ren K, Neese B, Lin M, Wang Q, et al. 'A dielectric polymer with high electric energy density and fast discharge speed', Science 313(5785) (2006) 334-7.
4. Cheng Yang, Yuanhua Lin, C.W. Nan, 'Modified carbon nanotube composites with high dielectric constant, low dielectric loss and large energy density', carbon 47 (2009) 1096-1101.
5. Hualan Wang , Qingli Hao , Xujie Yang , Lude Lu, Xin Wang ,' Effect of Graphene Oxide on the Properties of Its Composite with Polyaniline', ACS Appl. Mater. Interfaces, 2 (3) (2010) 821-828.
6. Qun Li, Qingzhong Xue , Qingbin Zheng, Lanzhong Hao, Xili Gao, 'Large dielectric constant of the chemically purified carbon nanotube/polymer composites', Materials Letters 62 (2008) 4229-4231.
7. E Kymakis, I Alexandou, G.A.J Amaratunga, Synthetic Metals, 'Single-walled carbon nanotube-polymer composites: electrical, optical and structural investigation', Synthetic Metals 127 (2002) 59-62.

8. Ranulfo Allen, Lijia Pan, Gerald G. Fuller, Zhenan Bao, 'Using in-Situ Polymerization of Conductive Polymers to Enhance the Electrical Properties of Solution-Processed Carbon Nanotube Films and Fibers', ACS Appl. Mater. Interfaces (2014).
9. Chuang Peng, Shengwen Zhang, Daniel Jewell, George Z. Chen, 'Carbon nanotube and conducting polymer composites for supercapacitors', Progress in Natural Science 18 (2008) 777–788.
10. Ashis K. Sarker, Jong-Dal Hong, 'Electrochemical reduction of ultrathin graphene oxide/polyaniline films for supercapacitor electrodes with a high specific capacitance', Colloids and Surfaces A: Physicochemical and Engineering Aspects 436 (2013) 967–974.
11. Nanjundan Ashok Kumar, Hyun-Jung Choi, Yeon Ran Shin, Dong Wook Chang, Liming Dai, Jong-Beom Baek, 'Polyaniline-Grafted Reduced Graphene Oxide for Efficient Electrochemical Supercapacitors', *ACS Nano* 6(2) (2012) 1715–1723.
12. Hualan Wang , Qingli Hao , Xujie Yang , Lude Lu, Xin Wang ,' Effect of Graphene Oxide on the Properties of Its Composite with Polyaniline', ACS Appl. Mater. Interfaces, 2 (3) (2010) 821–828.
13. Qingqing Zhang, Yu Li, Yiyu Feng, Wei Feng, 'Electropolymerization of graphene oxide/polyaniline composite for high-performance supercapacitor', Electrochimica Acta 90 (2013) 95–100
14. Zhu J, Gu H, Luo Z, Haldolaarachige N, Young DP, Wei S, Guo Z.,' Carbon nanostructure-derived polyaniline metacomposites: electrical, dielectric, and giant magnetoresistive properties', Langmuir 28(27) (2012) 10246-55.
15. Emer Lahiff, Carol Lynam, Niamh Gilmartin, Richard O'Kenned2, Dermot Diamond,' Review Article: The Increasing Importance of Carbon Nanotubes and Nanostructured Conducting Polymers in Biosensors', Anal Bioanal Chem 398 (2010) 1575–1589.

16. Moumita Kotal, Awalendra K. Thakur, Anil K. Bhowmick,' Polyaniline–Carbon Nanofiber Composite by a Chemical Grafting Approach and Its Supercapacitor Application', ACS Appl. Mater. Interfaces 5 (2013) 8374–8386.